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PROCESS FOR PREPARING NOVEL VINYL MONOMERS FROM
RICINOLEIC ACID AND MIXED FATTY ACIDS OF CASTOR OIL.

THE ALKALI AND CHEMICAL CORPORATION OF INDIA
LIMITED, of I.C.I. House, 34' Chowringhee Road,
Calcutta-700 071, West Bengal, India, an Indian
Company.

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

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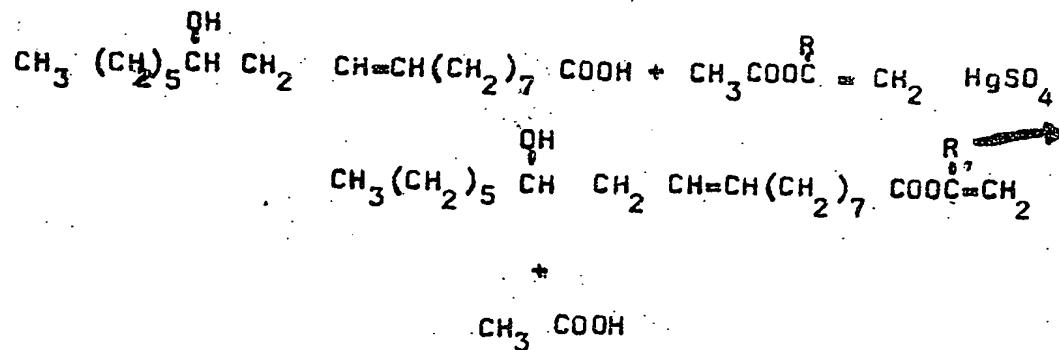
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The present invention relates to a process for preparing undehydrated vinyl monomers from ricinoleic acid, and their subsequent polymerisation in bulk, solution or emulsion.

Hitherto, all previous attempts reported in the literature to synthesise undehydrated vinyl monomers from ricinoleic acid have given rise to the dehydrated products.

However, we have now found that by the choice of a suitable catalyst, the hydroxyl group in the 12- position is preserved and thus the vinyl monomers resulting from ricinoleic acid are undehydrated.

It may be noted that the undehydrated vinyl derivative of ricinoleic acid is obtained by reacting ricinoleic acid in the presence of mercuric sulphate as a catalyst maintained or kept at room temperature for a period of 72 hours. The reaction scheme, by way of example, is illustrated below:-



wherein R is H or CH_3 .

According to the invention, there is provided a process for preparing undehydrated vinyl monomer which comprises synthesising a vinyl monomer of ricinoleic acid in the presence of

a suitable catalyst preferably mercuric sulphate whereby the OH group in the 12-position remains intact.

The vinyl monomers obtained according to the process of the present invention can be further homopolymerised or copolymerised with other suitable monomers in bulk, solution or emulsion, to give products which might find applications in the coating, paints, adhesives and surfactant industries.

According to the invention, monomers synthesis is exemplified as follows:-

Example

30 parts by weight of ricinoleic acid was reacted with 30 parts by weight of vinyl acetate in the presence of 1 part by weight of mercuric sulphate catalyst for seventy-two hours. At the end of the reaction the excess vinyl acetate was removed by distillation, the acetic acid formed in the reaction removed by treatment with base, and the pure products extracted into ether.

The product was characterised by infra-red spectroscopy.

Polymerisation Studies

Emulsion homopolymerisation of vinyl ricinoleate or copolymerisation with methyl methacrylate was carried out at 80°C for 3 hours, using suitable emulsifier blends, and a water soluble free radical initiator.

1 5 3 5 9 9

solution polymerisation of vinyl ricinoleate was carried out at 60°C in benzene, toluene or chlorinated solvents, with a free radical initiator.

Bulk polymerisation was achieved by thermal initiation.

Dated this 11th day of March, 1980.

Sd/-
(C.K. VIRMANI)
OF REMFRY & SON
AGENT FOR THE APPLICANTS.

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION
(Section-10)

Process for preparing novel vinyl monomers from
ricinoleic acid or mixed fatty acids of castor oil.

THE ALKALI AND CHEMICAL CORPORATION OF INDIA LIMITED,
of I.C.I. House, 34 Chouringhee Road, Calcutta-700 071,
West Bengal, India, an Indian Company.

The following specification particularly describes and ascertains the nature of this invention
and the manner in which it is to be performed:—

The present invention relates to a process for preparing novel vinyl monomers. More particularly, the invention relates to the preparation of novel vinyl monomers from ricinoleic acid or mixed fatty acids of castor oil.

Hitherto, all previous attempts reported in the literature to synthesise undehydrated vinyl monomers from ricinoleic acid have given rise to dehydrated products.

It is therefore an object of the present invention to retain the hydroxyl group in the 12 position in the ricinoleic acid molecule in tact.

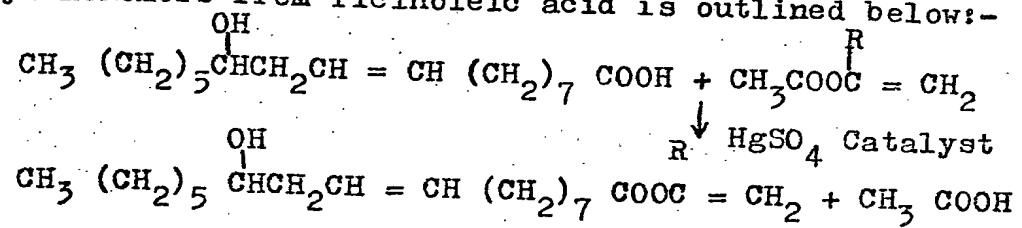
The advantage to have the preserved hydroxyl group makes the vinyl monomers resulting from ricinoleic acid very versatile in that further derivatisation can be carried on the hydroxyl group even after polymerisation.

We have now found that by the choice of a suitable catalyst and reaction conditions the hydroxyl group in the 12 position is preserved and thus the vinyl monomers resulting from the ricinoleic acid are undehydrated. We have also found that the novel vinyl monomers can be prepared from the fatty acids of castor oil since the latter is predominantly ricinoleic acid.

According to the invention there is provided a process for preparing novel vinyl monomer of ricinoleic acid or

mixed fatty acids of castor oil which comprises reacting ricinoleic acid or mixed fatty acids of castor oil with a vinyl ester of acetic acid of the formula $\text{CH}_3\text{COOC}-\text{CH}_2-\text{CH}_2-\text{R}$ wherein R is H or CH_3 , in the presence of a catalyst such as mercuric sulphate.

The reaction scheme showing the preparation of the vinyl monomers from ricinoleic acid is outlined below:-



where R is H or CH_3 .

When mixed fatty acids of castor oil are used, similar esterification reaction takes place simultaneously with the other fatty acids present, so that a mixture of vinyl esters containing predominantly vinyl ricinoleate is obtained.

The reaction may be carried out at temperatures ranging from 25 - 70°C for a period of time ranging from 72 hrs to 3 hours.

The vinyl monomers obtained according to the process of the present invention can be further homopolymerised or copolymerised with other suitable monomers in solution, emulsion or bulk to give products which find outlets in paints, adhesives and coatings industries. For instance,

the low molecular weight solution copolymers have good adhesive properties as well as serving as lacquers. The high molecular weight emulsion copolymers serve as the vehicle for emulsion paints.

The invention will now be described with reference to the following examples which should not be considered limitative:-

EXAMPLE 1

30 parts by weight of ricinoleic acid was reacted with 30 parts by weight of vinyl acetate in the presence of 1 part by weight of mercuric sulphate for 72 hours at room temperature. At the end of 72 hours, the excess unreacted vinyl acetate was removed by distillation under vacuum (20 mm of Hg). The acetic acid formed in the reaction as a product was removed by extracting the mixture of products (vinyl ricinoleate and acetic acid) with aqueous sodium carbonate solution. The aqueous layer was then separated thus removing the acetic acid and leaving the vinyl ricinoleate. The vinyl ricinoleate was then extracted with ether and any residual aqueous impurities separated, the ether was evaporated at 40°C thus leaving the pure vinyl ricinoleate. The yield obtained of pure vinyl ricinoleate by this method is about 80%. The product was characterised by infra-red spectroscopy. The typical hydroxyl absorption at about 3500 cm^{-1} and the vinyl absorption at 1645 cm^{-1} show that the undehydrated vinyl ricinoleate has been formed.

EXAMPLE 2

30 parts by weight of ricinoleic acid was reacted with 30 parts by weight of vinyl acetate in the presence of 1 part by weight of mercuric sulphate for 3 hours at 70°C. At the end of the three hours, the excess unreacted vinyl acetate was removed by distillation under vacuum (20mm of Hg). The acetic acid formed in the reaction as a product was removed by extracting the mixture of products (vinyl ricinoleate and acetic acid) with aqueous sodium carbonate solution. The aqueous layer was then separated thus removing the acetic acid and leaving the vinyl ricinoleate. The vinyl ricinoleate was then extracted with ether and any residual aqueous impurities separated. The ether was evaporated at 40°C thus leaving the pure vinyl ricinoleate. The yield obtained by this method of pure vinyl ricinoleate is about 90%. The product was characterised by infra-red spectroscopy. The typical hydroxyl absorption at about 3500 cm^{-1} and the vinyl absorption at 1645 cm^{-1} confirm that the undehydrated vinyl ricinoleate has been formed.

EXAMPLE 3

36 parts by weight of mixed fatty acids of castor oil were reacted with 30 parts by weight of vinyl acetate in the presence of 1.2 parts by weight mercuric sulphate for 3 hours at 70°C. At the end of three hours the excess unreacted vinyl acetate was removed by distillation under vacuum (20mm of Hg). The acetic acid formed in the reaction was removed by extracting the mixture of products with aqueous sodium bicarbonate solution. The aqueous layer was then separated leaving

the vinyl esters of the mixed fatty acids of castor oil. These vinyl esters were then extracted with ether and any residual aqueous impurities separated. The ether was evaporated at 40°C thus leaving the vinyl esters of the mixed fatty acids of castor oil. The yield obtained of these esters is about 90%.

The polymerisation studies with the above monomers is exemplified below:

The examples show solution homopolymerisation, solution copolymerisation and emulsion copolymerisation with monomers such as vinyl acetate, styrene and methyl methacrylate.

EXAMPLE 4

10 parts by weight of vinyl ricinoleate, 10 parts by weight of vinyl acetate, 0.4 parts by weight 2,2'-azobisisobutyronitrile (free radical initiator), 80 parts by weight ethyl acetate, were put into a 250cc round bottomed flask, and the copolymerisation was carried out at 80°C in a nitrogen atmosphere for 5 hours. The copolymer may be used as such or the solvent evaporated off yielding a solid copolymer.

The conversion of monomer to polymer was found to be 58%.

The average molecular weight of the copolymer was found to be 6500. Glass transition studies were carried out on the polymer. Only one transition was observed indicating that a genuine copolymer had been formed and not a mixture of two

homopolymers.

EXAMPLE 5

20 parts by weight vinyl ricinoleate, 0.4 parts by weight of 2,2'-azobisisobutyronitrile (free radical initiator), 80 parts by weight ethyl acetate were put into a 250cc round bottomed flask, and the homopolymerisation carried out at 80°C in a nitrogen atmosphere for 5 hours.

The conversion of monomer to polymer was found to be 57%.

EXAMPLE 6

16 parts by weight of styrene, 4 parts by weight of vinyl ricinoleate, 0.4 parts by weight of 2,2'-azobisisobutyronitrile (free radical initiator), 80 parts by weight of ethyl acetate were put into a 250cc round bottomed flask and copolymerisation was carried out at 80°C, in a nitrogen atmosphere for 5 hours. The copolymer may be used as such or the solvent evaporated off yielding the solid copolymer.

The conversion of monomer to polymer was found to be 72%. The average molecular weight of the copolymer was found to be 8000.

EXAMPLE 7

The emulsion copolymerisation of the vinyl esters of the mixed fatty acids of castor oil with methyl methacrylate was carried out as described below.

87 parts by weight of methyl methacrylate, 85 parts by weight of vinyl esters of mixed fatty acids of castor oil, 2 parts by weight of methacrylic acid, 16 parts by weight of a nonionic surfactant and 5 parts by weight of an anionic surfactant, were mixed together. To this was added 1.6 parts

by weight of potassium persulphate (initiator), and 0.4 parts by weight of borax dissolved in 16 parts by weight of water along with 175 parts by weight of tap water containing 0.9 parts by weight of sodium carboxy methyl cellulose. The entire mixture was stirred at 220 r.p.m. in a 500ml round bottomed flask in an atmosphere of nitrogen at 85°C. The reaction was carried out for 4 1/2 hours. The conversion of monomer to polymer was found to be 70%. The average molecular weight of the polymer was found to be 120,000.

EXAMPLE 8

Bulk copolymerisation of vinyl ricinoleate with methyl methacrylate was carried out using the following procedure:-

10 parts by weight of methyl methacrylate, 10 parts by weight of vinyl ricinoleate, with 0.4 parts by weight of 2,2'-azobisisobutyronitrile were placed in a 100cc round bottomed flask. The polymerisation was carried out under nitrogen at 80°C.

After $\frac{1}{2}$ hour a viscous liquid results which is the bulk copolymer final product.

We Claim:-

1. A process for the preparation of novel vinyl monomers of ricinoleic acid or mixed fatty acids of castor oil which comprises reacting ricinoleic acid or mixed fatty acids of castor oil with a vinyl ester of acetic acid of the formula $\text{CH}_3\text{COOC} - \text{CH}_2$, wherein R is H or CH_3 , in the presence of a catalyst such as mercuric sulphate.
2. A process as claimed in claim 1, where the reaction is carried out at a temperature ranging from 25°C to 70°C for a period of time ranging from 72 hours to 3 hours.
3. A process for the preparation of novel vinyl monomers substantially as herein described with reference to the foregoing examples.

Dated this 4th day of June, 1981.

Sd/-
(A. GABRIEL)
OF REMFRY & SON
AGENT FOR THE APPLICANTS.

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GOVERNMENT OF INDIA, THE PATENT OFFICE
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CALCUTTA-700017.

Complete Specification No. 154647 dated 12th August, 1981.

Application and Provisional Specification No. 907/Cal/81 dated 12th Aug., 1981.

Acceptance of the complete specification advertised on 24th November, 1984.

Index at acceptance— 32F3b [1x(1)]

International Classification— C11C 3/10.

Process for preparing derivatives of castor oil

The Alkali and Chemical Corporation of India Limited,
an Indian Company, of ICI House, 34 Chowringhee Road, Calcutta-700071,
West Bengal, India.

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

This invention has been conceived by Dr. Annoottam Ghosh.

The present invention relates to a process for preparing novel derivatives of castor oil, and their subsequent polymerisation in emulsion, solution and bulk.

The polymers which are also novel, have potential applications in the adhesives and surface coatings industries. In particular, the solution copolymers have outlets as adhesives or lacquers. The emulsion copolymers are useful as vehicles for emulsion paints.

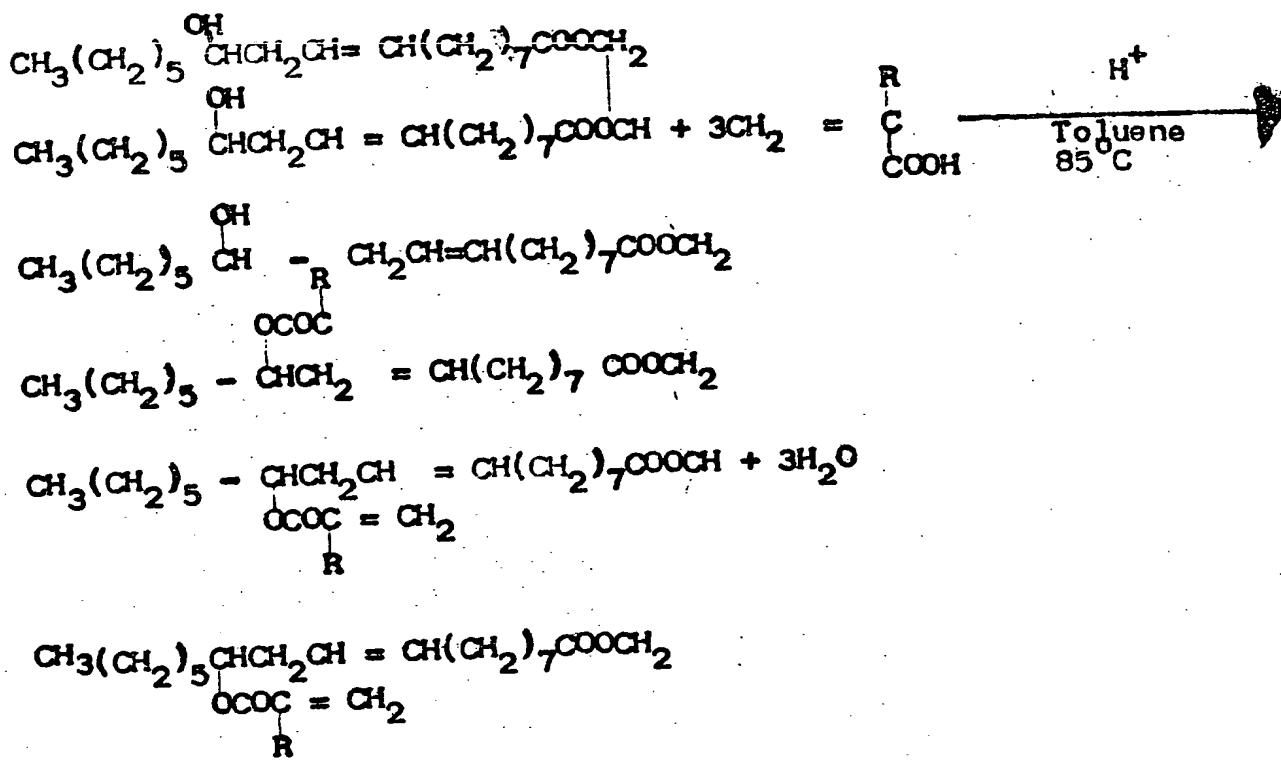
These polymerisable derivatives of castor oil may be synthesised by reacting castor oil with an acrylic acid of the following formula:



where R is H or CH_3

in the presence of a trace a trace of mineral acid as catalyst. The water liberated during the reaction is removed continuously by azeotropic distillation with toluene at about 85°C as outlined below in the reaction scheme.

The process for preparation of these novel derivatives is illustrated by the following reaction scheme. In this scheme, castor oil is represented by the triglyceride of ricinoleic acid, which constitutes about 85% of triglycerides present in castor oil. The remaining triglycerides take no part in the esterification reaction.

Reaction Scheme :ACRYLATED OR METHACRYLATED CASTOR OIL

R is H or CH_3

The number of moles of the acrylic acid or methacrylic acid can be varied between 0 moles to 3 moles, accordingly the degree of substitution varies between 0 and 2.8.

EXAMPLE 1

1864 parts by weight of castor oil was mixed with 432 parts by weight of acrylic acid and to this was added 92 parts by weight of toluene. A trace of concentrated sulfuric acid (0.01% with respect to the castor oil) was

added to catalyse the reaction. 0.1% hydroquinone was added as an inhibitor, so that the homopolymerisation of acrylic acid is suppressed and the whole reaction mixture was heated in a three-necked round bottom flask equipped with a mechanical stirrer and the Dean-Stark assembly. The water formed during the reaction formed an azeotrope with toluene which came over at 85°C. The total amount of water collected was 108 ml. which was equal to the stoichimometric amount. The reaction was carried out for 4½ hours.

The yield was found to be about 95% and the product was characterised by infra-red spectroscopy. The hydroxyl values indicated the functionality of the product to be approximately 2.8.

EXAMPLE 2

1864 parts by weight of castor oil was mixed with 206.4 parts by weight of methacrylic acid, in a three-necked round bottom flask equipped with a mechanical stirrer and the Dean-Stark assembly. A trace of concentrated sulfuric acid (0.01%) was added as a catalyst. 0.1% of hydroquinone was added as an inhibitor so that the homopolymerisation of methacrylic acid is suppressed, and 30.3 parts by weight of toluene was added to form an azeotrope with the water formed during the course of the reaction. The azeotrope started coming over at 85°C. The total amount of water collected was 36 ml. The reaction was carried out for 5 hours. The yield was found to be about 95% and the product was characterised

by infra-red spectroscopy. The functionality of the product was found to be approximately 1.8.

POLYMERISATION STUDIES

Emulsion homopolymerisation or copolymerisation of the above monomers with common cinnyl monomers such as methyl methacrylate, styrene or cinnyl acetate was carried out with a free radical initiator at 85°C for 4 hours.

Solution polymerisation of the above monomers was carried out in the usual organic solvents such as ethyl acetate, ethanol, acetone at 70-80°C with a free radical initiator.

EXAMPLE 3

SOLUTION COPOLYMERISATION

6 parts by weight of acrylated castor oil and 14 parts by weight of methyl methacrylate and 0.8 parts by weight of 2,2'-azobis-iso butyronitrile and 80 parts by weight ethyl acetate were heated together for 4½ hours at 78°C in N₂ atmosphere to give a solution copolymer of average molecular weight of 14,000 and conversion of monomer to polymer was found to be 91.2% Glass transition measurements were carried out on the polymers. Only one transition was observed indicating that a genuine copolymer had been formed and not a mixture of two homopolymers. The solution copolymer

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